Rare Metal Materials and Engineering
Volume 49, Issue 10, October 2020
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2020, 49(10): 3332-3337.

ARTICLE

Thermodynamic Database for Mo-RE Binary Alloy Systems

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Abstract: Thermodynamic database of the Mo-RE (RE: Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm, Yb, Lu) system was developed for the design of the Molybdenum-based refractory alloys. The thermodynamic calculation and optimization of Mo-RE binary system were performed using the calculation of phase diagrams (CALPHAD) method on the basis of experimental data including phase equilibrium and thermodynamic properties. The Gibbs energy of the liquid and solid solution phases was described by the sub-regular solution model, whereas that of the gas phases was described by the ideal gas model. The results show that a set of self-consistent thermodynamic parameters are obtained that reasonably describe the thermodynamic properties of the Mo-RE binary systems. A good agreement between calculated results and experimental data is achieved. The utility of this database is demonstrated in the thermodynamic calculation examples of the mixing enthalpy of liquid phase in the Mo-Ce and Mo-Pr system. Also, the 1200, 1300, 1400 °C isothermal section diagrams of the Mo-Ho-Tb system and related property diagrams like phase fraction of desired phases are depicted. Meanwhile, the Mo-Cu-Er ternary phase equilibrium section from 800 °C to 1000 °C is extrapolated. The results show fairly good prediction and provide much-needed information for the alloy design of the molybdenum-based refractory materials.

Key words: Mo-RE alloys; rare metals; thermodynamic database; phase diagram

Mo-RE (RE: rare earth metals) alloys, instead of molybdenum, have been applied in the fields of blast furnace and electronic tubes due to their better service performance[1-4]. To better understand the internal relationship between microstructure and properties, it is very important to develop phase diagram thermodynamic calculation and to construct the thermodynamic databases of the Mo-RE alloys.

However, research on the optimization and calculation of the Mo-RE binary systems is rather limited. This research developed a thermodynamic database for the phase diagrams of the Mo-RE (RE: Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm, Yb, Lu) binary systems. The thermodynamic optimization and calculation were achieved by a group of self-consistent thermodynamic parameters based on the CALPHAD method and experimental data of phase equilibrium and thermodynamic properties.

1 CALPHAD Method

The CALPHAD method is a powerful tool to design multicomponent alloys with less time and lower cost. Essential procedures of this method are: first, investigate and evaluate archives of relevant phase diagrams and their thermodynamic information; second, select suitable thermodynamic models according to the structural characteristics of each phase and set up Gibbs energy expression of each phase in the modeled system; third, estimate undetermined thermodynamic parameters using optimal-selected phase diagram, thermodynamic data and phase diagram calculation software; fourth, give certain weight to the data according to the experimental error and personal judgment in the procedure of optimization. The error between the calculated results and experimental results will finally decrease till the majority of

Received date: October 29, 2019
Foundation item: Open Fund of State Key Laboratory of Baiyunobo Rare Earth Resource Researches and Comprehensive Utilization; National Natural Science Foundation of China (51771158)
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the data fit the experimental information. Thus, a group of self-consistent thermodynamic parameters that rationally describe the free energies of each phase was acquired. Furthermore, reference parameters from binary and ternary components with key experimental data could be a confidential guide in the extrapolation of phase diagram and thermodynamic properties of practical multi-component systems.

2 Thermodynamic Models

2.1 Pure elements

The Gibbs free energy of pure elements of Mo-RE systems is referred to the enthalpy of elements in standard element reference (SER) state at 298.15 K and 101 325 Pa (H_i^{SER} (298.15 K)). It is expressed as a function of temperature in the following form:

$$\begin{aligned} {}^{0}G_i(T) &= G_i(T) - H_i^{\mathrm{SER}}(298.15\ \mathrm{K}) \\ &= a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + \sum_n g_n T^n \end{aligned} \quad (1)$$

where a~f and g_n are coefficients and n represents a set of integers. The corresponding coefficients in the present work are taken from the SGTE pure element database compiled by Dinsdale[5].

2.2 Liquid and solid solution phases

The Gibbs free energy of the liquid and solution phases is described by a subregular solution model[6], which is expressed per mole as:

$$G_m^{\phi} = \sum_i {}^{0}G_i^{\phi} x_i + RT\sum_i x_i \ln x_i + {}^{E}G_m^{\phi} \quad (2)$$

where x_i is the mole fraction of component i in ϕ phase; ${}^{0}G_i^{\phi}$ is the standard Gibbs free energy of pure element i in ϕ phase; $RT\sum_i x_i \ln x_i$ denotes the ideal Gibbs free energy of mixing and R is the gas constant; ${}^{E}G_m^{\phi}$ is the excess free energy of ϕ phase，which is expressed by the Redlich-Kister polynomial[7] as:

$${}^{E}G_m^{\phi} = x_i x_j[{}^{0}L_{i,j}^{\phi} + {}^{1}L_{i,j}^{\phi}(x_i - x_j) + {}^{2}L_{i,j}^{\phi}(x_i - x_j)^2 + \cdots] \quad (3)$$

where ${}^{m}L_{i,j}^{\phi}$ is the interaction parameter between i and j atoms and is expressed as:

$${}^{m}L_{i,j}^{\phi} = a + bT + cT\ln T \quad (4)$$

where a, b and c are preparative optimization thermodynamic parameters.

2.3 Gas phase

Gas phase boundary line calculation is involved in Mo-Sm, Mo-Eu and Mo-Tm binary phase diagrams. The Gibbs energy of these binary systems is described as ideal gas model in this research, which can be expressed as:

$$G^{\mathrm{gas}} = \sum_i x_i {}^{0}G_i^{\mathrm{gas}} + RT\sum_i x_i \ln x_i + RT\ln\left(\frac{p}{p_0}\right) \quad (5)$$

where x_i is the mole fraction of gas component i; ${}^{0}G_i^{\mathrm{gas}}$ is the standard Gibbs free energy of pure element i, whose value is entirely taken from Dinsdale's SGTE element database; R is the gas volume constant; p_0 is the standard atmosphere pressure, p is the actual pressure condition where the system situates.

3 Application of Thermodynamic Database

In the present research, Mo-RE binary phase diagrams are optimized and calculated using available experimental data including phase diagram, and related thermodynamic information. Concrete work has been accomplished using the Thermo-Calc software. There is a good consistency between calculated results and experimental data. Consequently, a thermodynamic database of Mo-RE binary alloy phase diagrams is basically established. This database can provide a variety of information of phase equilibrium and thermodynamic properties such as calculation of stable and metastable phases, and thermodynamic properties (formation enthalpy, liquid mixing enthalpy, Gibbs free energy). Meanwhile, it also serves as a guidance extrapolation and estimation of phase equilibrium of multicomponent molybdenum alloys in terms of the thermodynamic calculations.

3.1 Calculation of Mo-RE binary phase diagrams

Eleven Mo-RE binary phase diagrams are calculated using the present Mo-RE binary thermodynamic database for refractory materials, as shown in Fig.1[8-18]. Fig.1a~1k show the calculated phase diagrams of Mo-RE (RE: Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm, Yb, Lu) compared with the available experimental data. The comparison between the experimental data and the calculated results show that the thermodynamic data from the optimized database reproduces every Mo-RE phase diagram well. And there are certain similarities and regularities in phase equilibrium and liquidus shape in most Mo-RE binary phase diagrams.

Eleven Mo-RE binary systems can be divided into two categories according to their characteristics at the high temperature. One is so-called liquid-liquid phase separation type while the other is the gas-containing one. There are typical liquid-liquid phase separation phenomena in Mo-Ce (Fig.1a), Mo-Pr (Fig.1b), Mo-Nd (Fig.1c), Mo-Tb (Fig.1f), Mo-Ho (Fig.1g), Mo-Er (Fig.1h), Mo-Yb (Fig.1j) and Mo-Lu (Fig.1k) systems. As a special case, the metastable miscibility gap in the Mo-Lu system is presented as broken lines. Apart from these, the rest Mo-Sm (Fig.1d), Mo-Eu (Fig.1e) and Mo-Tm (Fig.1i) systems are gas-containing types. The gas phase boundaries were calculated based on the ideal gas model. These calculated results agree well with the experimental phase diagrams.

3.2 Calculation of thermodynamic properties

Related reports including thermodynamic data of Mo-RE binary systems have not been found. Thermodynamic properties of each binary system can be estimated based on the Mo-RE binary system database. As an example, the liquidus mixing enthalpy of Mo-Ce and Mo-Pr at 2600 °C is calculated, shown in Fig.2a and 2b, respectively. It can be

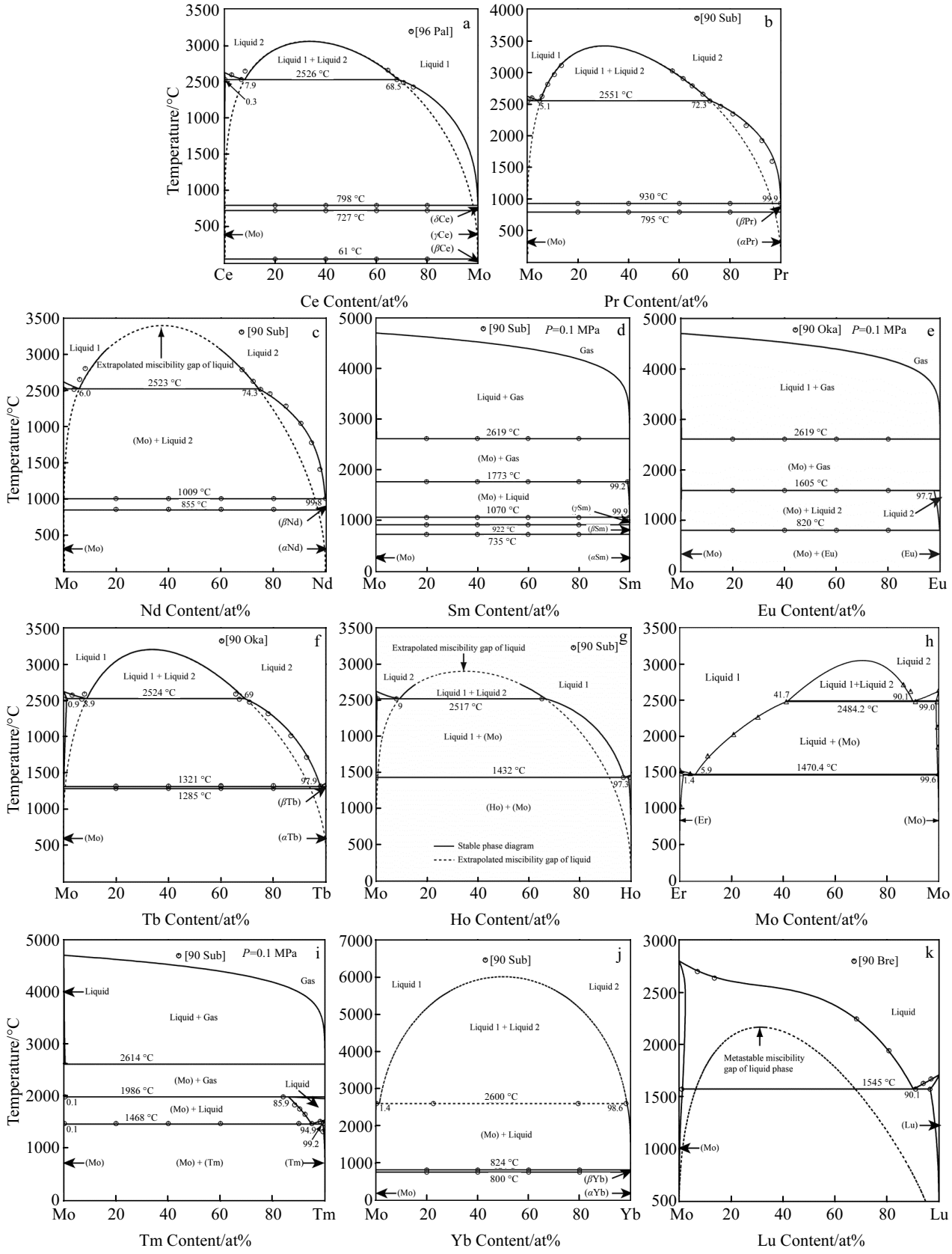

Fig.1 Calculated phase diagrams of Mo-RE binary system compared with the experimental data[8-18]: (a) Mo-Ce, (b) Mo-Pr, (c) Mo-Nd, (d) Mo-Sm, (e) Mo-Eu, (f) Mo-Tb, (g) Mo-Ho, (h) Mo-Er, (i) Mo-Tm, (j) Mo-Yb, and (k) Mo-Lu

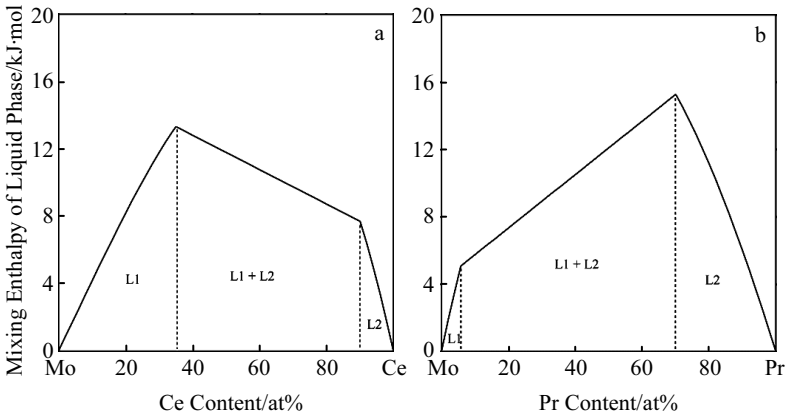

Fig.2 Calculated mixing enthalpy of liquid phase in Mo-Ce (a) and Mo-Pr (b) system at 2600 °C

seen in Fig.2 that all the values calculated regarding the liquidus mixing enthalpy of Mo-Ce and Mo-Pr are positive and the two points of inflexion indicate the boundaries of the liquidus phase separation. Thus, is it evident that the thermodynamic parameters in the database can be used to calculate both phase equilibrium and thermodynamic properties of different phases in the Mo-RE systems.

3.3 Calculation of relevant ternary phase diagrams

The Mo-RE binary alloy database established in the present research can provide crucial information for the thermodynamic optimization and calculation of multicomponent systems. In the follows, several examples are depicted for showing the advantages of the developed database.

Firstly, the ternary phase equilibrium of Mo-based ternary systems including the isothermal and vertical section diagrams, property diagrams, etc, can be extrapolated when there are no ternary compounds and the solubility of a third element in the binary compounds can be negligible. Fig.3 presents the calculated isothermal sections of the Mo-Ho-Tb ternary system at 1200, 1300, 1400 °C. The vertical section diagrams at composition of 10 at% Ho are also calculated and shown in Fig.4a. It clearly shows that there is a liquid-liquid phase separation above 2500 °C. On this basis, two ternary compositions of Mo-10Ho-10Tb and Mo-20Ho-10Tb (at%) are selected. And their phase mole fractions as a function of temperature are calculated, as shown in Fig.4b and 4c, respectively.

Besides, according to reports concerning the thermodynamic parameters of Cu-Mo and Cu-Er and the optimization of the Mo-Er systems, extrapolated calculation of Mo-Cu-Er ternary system was also performed using the CALPHAD method. Fig.5 shows the calculated isothermal sections of Mo-Cu-Er System at 800, 900 and 1000 °C. Phase equilibrium of the Mo-Cu-Er ternary system is relatively simple since intermetallic phases exist only in the Cu-Er binary system. From the temperature of 900 °C, as shown in Fig.5b and 5c, the rich Cu-Er region firstly generates the liquidus region and the region enlarges with the increase of the temperature. Due to the lack of information in the Mo-Cu-Er and the Mo-Ho-Tb ternary phase diagrams and the thermodynamic data, the above-mentioned extrapolation remains to be verified by further experiments. Yet these calculation results can still provide certain theoretical guidance in terms of the alloy design and the materials development.

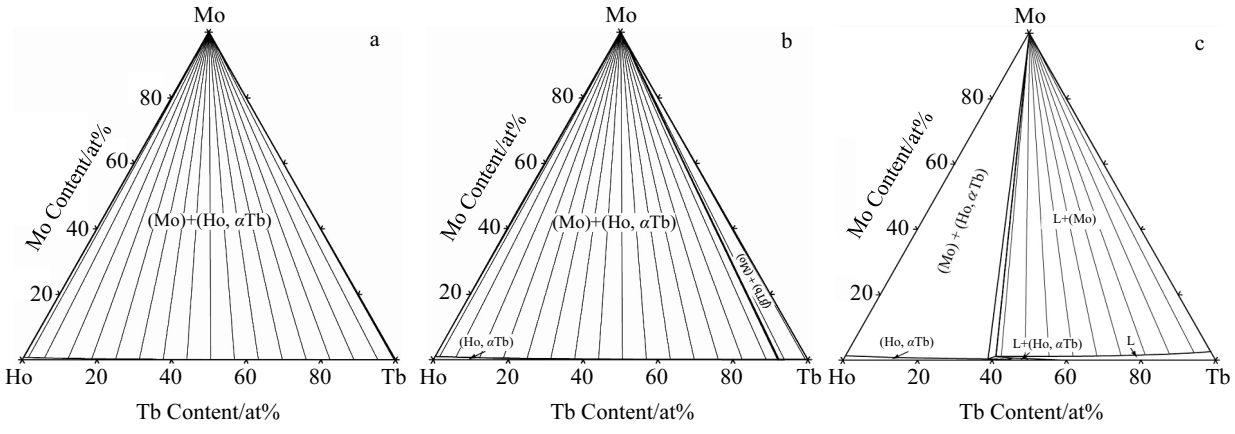

Fig.3 Calculated isothermal sections of the Mo-Ho-Tb ternary system at different temperatures: (a) 1200 °C, (b) 1300 °C, and (c) 1400 °C

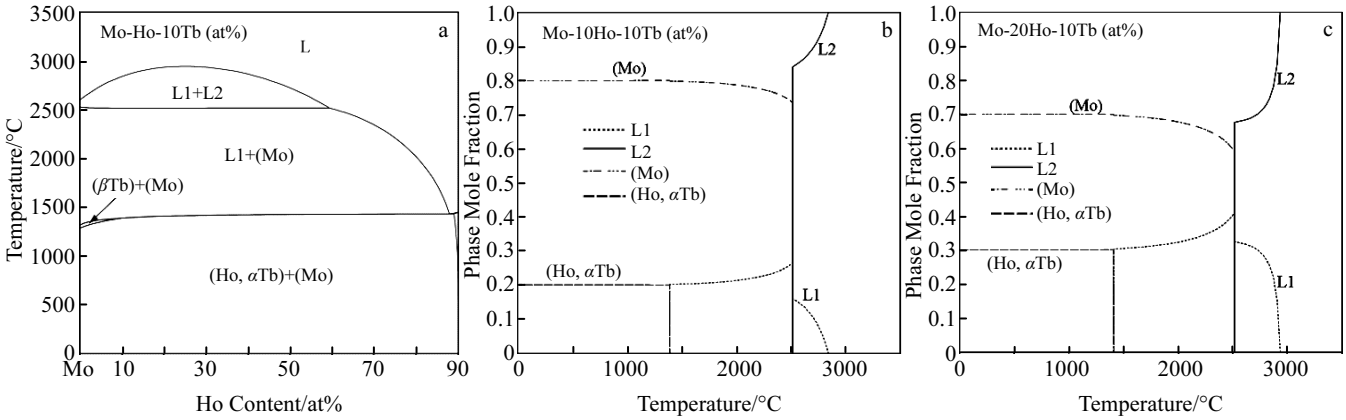

Fig.4 Calculated thermodynamic diagrams of Mo-Ho-Tb ternary system: (a) vertical section of the $Mo_{90}Tb_{10}$-$Ho_{90}Tb_{10}$ Pseudo binary system; phase mole fraction as a function of temperature for alloy $Mo_{80}Ho_{10}Tb_{10}$ (b) and $Mo_{70}Ho_{20}Tb_{10}$ (c)

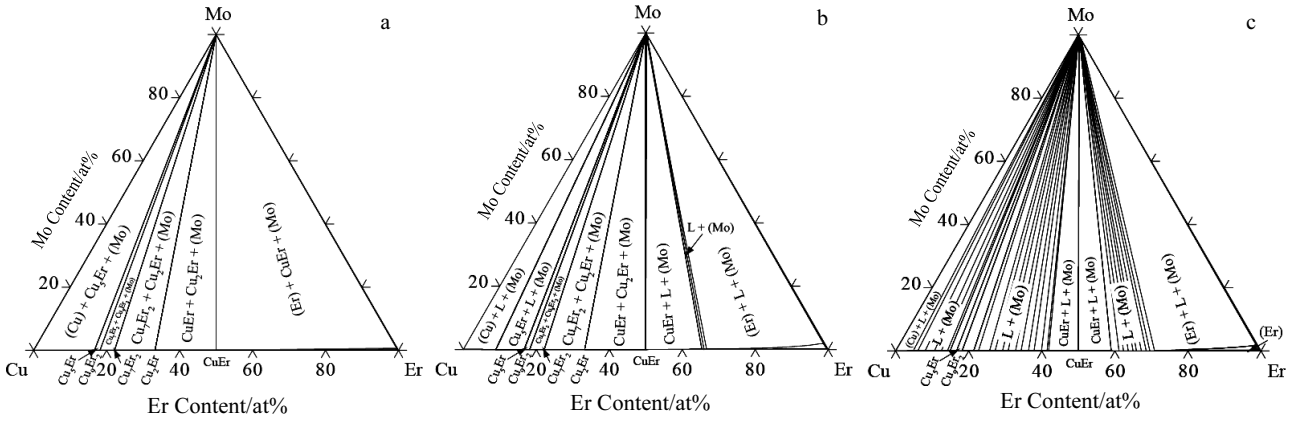

Fig.5 Calculated isothermal sections of the Mo-Cu-Er ternary system at different temperatures: (a) 800 °C, (b) 900 °C, and (c) 1000 °C

4 Conclusions

1) A thermodynamic database for the Mo-RE (RE: Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm, Yb, Lu) alloy systems is developed based on the experimental phase diagrams and related thermodynamic information.

2) This database can provide much-needed information such as phase diagrams and thermodynamic properties for the materials design.

References

1 Liu G, Zhang G J, Jiang F *et al*. *Nature Materials*[J], 2013, 12(4): 344

2 Cockeram B V. *Materials Science and Engineering A*[J], 2010, 528(1): 288

3 Klopp W D. *Journal of the Less-Common Metals*[J], 1975, 42(3): 261

4 Cockeram B V. *Metallurgical and Materials Transactions A*[J], 2005, 36(7): 1777

5 Dinsdale. *SGTE Data for Pure Elements*[J], 1991, 15(4): 317

6 Hardy H K. *Acta Metallurgica*[J], 1953, 1(2): 202

7 Redlich O, Kister A T. *Ind Eng Chem*[J], 1948, 40(2): 345

8 Palenzona A, Cirafici S. *Journal of Phase Equilibria*[J], 1996, 17(1): 57

9 Predel B. *Mo-Pr* (*Molybdenum-Praseodymium*)[M]. Berlin: Springer, 1997

10 Predel B. *Mo-Nd (Molybdenum-Neodymium)*[M]. Berlin: Springer, 1997

11 Predel B. *Mo-Sm (Molybdenum-Samarium): Datasheet from Landolt-Börnstein-Group IV Physical Chemistry · Volume 5H: "Li-Mg-Nd-Zr" in Springer Materials*[M]. Berlin: Springer-Verlag, 1997

12 Predel B. *Eu-Mo (Europium-Molybdenum): Datasheet from Landolt-Börnstein-Group IV Physical Chemistry · Volume 5E: "Dy-Er-Fr-Mo" in Springer Materials*[M]. Berlin: Springer-Verlag, 1995

13 Predel B. *Mo-Tb (Molybdenum-Terbium): Datasheet from Landolt-Börnstein-Group IV Physical Chemistry · Volume 5H: "Li-Mg-Nd-Zr" in Springer Materials*[M]. Berlin: Springer-Verlag, 1997

14 Predel B. *Ho-Mo (Holmium-Molybdenum): Datasheet from*

Landolt-Börnstein-Group IV Physical Chemistry · Volume 5G: "Hg-Ho-La-Zr" in Springer Materials[M]. Berlin: Springer-Verlag, 1995

15 Predel B. *Mo-Yb (Molybdenum-Ytterbium): Datasheet from Landolt-Börnstein-Group IV Physical Chemistry · Volume 5H: "Li-Mg-Nd-Zr" in Springer Materials*[M]. Berlin: Springer-Verlag, 1995

16 Predel B. *Lu-Mo (Lutetium-Molybdenum): Datasheet from Landolt-Börnstein-Group IV Physical Chemistry · Volume 5H: "Li-Mg-Nd-Zr" in Springer Materials*[M]. Berlin: Springer-Verlag, 1995

17 Predel B. *Mo-Tm (Molybdenum-Thulium)*[M]. Berlin: Springer, 1997

18 Boer F R D, Dijkman W H, Mattens W C M *et al*. *Journal of the Less-Common Metals*[J], 1979, 64(2): 241

Mo-RE 二元合金相图的热力学数据库

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摘　要：利用 CALPHAD 方法，选择和建立合理的热力学模型，并结合相平衡及热力学性质的相关信息，对 Mo-RE (RE：Ce, Pr, Nd, Sm, Eu, Tb, Ho, Er, Tm, Yb, Lu)各二元系相图进行了热力学优化与计算。其中，液相和端际固溶体相的 Gibbs 自由能采用亚正规溶体模型描述，气相的 Gibbs 自由能采用理想气体模型描述。计算结果与实验数据取得了良好的一致性，最终得到了一组自洽的合理描述 Mo-RE 二元系各相自由能的热力学参数，建立了 Mo-RE 二元合金相图的热力学数据库。该热力学数据库可以提供相平衡及热力学性质等多种信息，为外推计算三元以及更多组元体系的相平衡提供理论基础，并为相关体系的合金设计及制备提供重要的理论指导。

关键词：Mo-RE 合金；稀土金属；热力学数据库；相图

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